Sr but other stuff

(12) **EUROPEAN PATENT APPLICATION**

(84) Designated Contracting States:
CH DE GB LI

(30) Priority: 12.08.1994 JP 190489/94

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(54) **Interconnector material for electrochemical cells**

(57) An interconnector material for use in electrochemical cells having Y_2O_3-stabilized ZrO_2 as a solid electrolyte, said interconnector material comprising a lanthanum chromite material of the following general formula:

$$(La_{1-x}Sr_x)(Cr_{1-y}M_y)O_3,$$
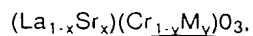
where M is Zr or Ti, x is in the range of 0.1 to 0.2, and y is in the range of 0.05 to 0.2.

EP 0 696 824 A1

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a lanthanum chromite material which can be advantageously used as an interconnector material in electrochemical cells such as solid-oxide fuel cells and solid-electrolyte steam electrolyzers.

2. Description of the Related Art

For example, in solid-oxide fuel cells (hereinafter abbreviated as SOFCs) or solid-electrolyte fuel cells, interconnectors are used as connecting members for combining a plurality of single cells to raise the total voltage and thereby obtain high electric power. Such interconnectors function not only to provide electrical connection, but also to separate the oxidizing gas (air) from the reducing gas (fuel) at elevated temperatures. Accordingly, refractory metals having a high melting point and perovskite type oxides, such as lanthanum chromite doped with Mg, Ca or Sr, have been used as interconnector materials.

Since the operating temperature of SOFCs is as high as 1,000°C or so, even high-melting metals form an oxide during long-term use in an oxidizing atmosphere. This is undesirable in that their surfaces come to have electrical insulating properties and thus exhibit poor electric conduction.

On the other hand, lanthanum chromite which is an oxide is stable in an oxidizing atmosphere, but has the disadvantage that its electric conductivity is low and some characteristics thereof, such as electric conductivity, change as a result of reduction in a reducing atmosphere. For this reason, lanthanum chromite has been doped with an alkaline earth metal, such as Mg, Ca or Sr, in order to enhance its electric conductivity. When lanthanum chromite is doped with Mg, Ca or Sr, its electric conductivity becomes higher in the order mentioned.

Moreover, since an SOFC is an assembly consisting of a solid electrolyte [i.e., YSZ (Y_2O_3-stabilized ZrO_2 or yttria-stabilized zirconia)], electrodes, such as oxygen electrodes and fuel electrodes, and interconnectors, the coefficient of thermal expansion of the interconnectors needs to match with that of YSZ, which forms a base. From this point of view, lanthanum chromite doped with Sr has a coefficient of thermal expansion of the order of 10×10^{-6} °C^{-1} which is almost equal to that of the solid electrolyte YSZ. Accordingly, lanthanum chromite doped with Sr which has a high electric conductivity and a coefficient of thermal expansion almost equal to that of the solid electrolyte YSZ has been used as an interconnector material for SOFCs.

Observing the behavior of lanthanum chromite doped with Sr in a reducing atmosphere, however, it has been found that a relatively high degree of expansion is caused by reduction. This is presumed to be responsible for deformation and cracking of the interconnectors, and delamination of the electrodes.

SUMMARY OF THE INVENTION

In view of the above-described technical level, an object of the present invention is to provide an interconnector material comprising a lanthanum chromite material which shows low reductive expansion, a high electric conductivity, and a coefficient of thermal expansion close to that of YSZ (i.e., 10.2×10^{-6} °C^{-1}).

The present invention provides an interconnector material for use in electrochemical cells having Y_2O_3-stabilized ZrO_2 as a solid electrolyte, comprising a lanthanum chromite material of the following general formula:

$$(La_{1-x}Sr_x)(Cr_{1-y}M_y)O_3,$$
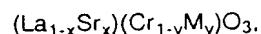
where M is Zr or Ti, x is in the range of 0.1 to 0.2, and y is in the range of 0.05 to 0.2.

According to the present invention, lanthanum chromite ($LaCrO_3$) is modified by replacing a portion of La by Sr and further replacing a portion of Cr by Zr or Ti. The resulting lanthanum chromite materials can prevent expansion in a high-temperature reducing atmosphere while retaining a high electric conductivity and a high coefficient of thermal expansion, and are hence useful as interconnector materials. Specifically, in the present invention, Sr is used as a doping element for lanthanum chromite, and zirconia or titania is further added thereto. As a result, there can be obtained a material having a high electric conductivity, a coefficient of thermal expansion of around 10×10^{-6} °C^{-1}, which is relatively high for ceramics, and a very low amount of expansion of about 0.1% or less as caused by the release of oxygen in a high-temperature reducing atmosphere.

In order to prevent the expansion of a lanthanum chromite material during reduction while maintaining its coefficient of thermal expansion at the same level as that of YSZ and without reducing its electric conductivity appreciably, the present invention involves adding zirconia or titania to lanthanum chromite in which a portion of La has been replaced by Sr as a solute element. This stabilizes the trivalent chromium and thereby makes it possible to minimize its expansion upon reduction.

For example, when 15% of La in lanthanum chromite of the formula $LaCrO_3$ is replaced by Sr, its electric conductivity at 1,000°C is as high as 30 S·cm^{-1}. Moreover, the coefficient of thermal expansion of this material is of the order of 10×10^{-6} °C^{-1} and almost equal to that of YSZ forming the main component of SOFCs. However, this material exhibits a high degree of expansion during reduction and its use has been limited thereby. According to the present invention, the requirements of interconnectors for use in SOFCs (i.e., a coefficient of thermal expansion almost equal to that of YSZ, a high electric conductivity, and the minimization of expansion during

by reduction) can be met by further replacing a portion of Cr by Zr or Ti.

The interconnector material of the present invention has a composition represented by the following general formula: $(La_{1-x}Sr_x)(Cr_{1-y}M_y)O_3$, where M is Zr or Ti, x is in the range of 0.1 to 0.2, and y is in the range of 0.05 to 0.2. These ranges of the x and y values have been determined so as to give a value of reductive expansion of not greater than 0.13% which is within acceptable limits for the deformation and cracking of interconnectors, an electric conductivity of not less than 10 S·cm^{-1} which is suitable for the practical use as interconnectors, and a coefficient of thermal expansion of 9 to 10.5 x 10^{-6} °C^{-1} which is close to that of YSZ.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing changes in the reductive expansion of the $(La_{1-x}Sr_x)(Cr_{1-y}Zr_y)O_3$ material of the present invention when x was fixed at 0.2 and y was varied;

Fig. 2 is a graph showing changes in the electric conductivity of the $(La_{1-x}Sr_x)(Cr_{1-y}Zr_y)O_3$ material of the present invention when x was fixed at 0.2 and y was varied;

Fig. 3 is a graph showing changes in the coefficient of thermal expansion of the $(La_{1-x}Sr_x)(Cr_{1-y}Zr_y)O_3$ material of the present invention when x was fixed at 0.2 and y was varied;

Fig. 4 is a graph showing changes in the reductive expansion of the $(La_{1-x}Sr_x)(Cr_{1-y}Zr_y)O_3$ material of the present invention when y was fixed at 0.1 and x was varied;

Fig. 5 is a graph showing changes in the electric conductivity of the $(La_{1-x}Sr_x)(Cr_{1-y}Zr_y)O_3$ material of the present invention when y was fixed at 0.1 and x was varied;

Fig. 6 is a graph showing changes in the coefficient of thermal expansion of the $(La_{1-x}Sr_x)(Cr_{1-y}Zr_y)O_3$ material of the present invention when y was fixed at 0.1 and x was varied;

Fig. 7 is a graph showing changes in the reductive expansion of the $(La_{1-x}Sr_x)(Cr_{1-y}Ti_y)O_3$ material of the present invention when x was fixed at 0.2 and y was varied;

Fig. 8 is a graph showing changes in the electric conductivity of the $(La_{1-x}Sr_x)(Cr_{1-y}Ti_y)O_3$ material of the present invention when x was fixed at 0.2 and y was varied;

Fig. 9 is a graph showing changes in the coefficient of thermal expansion of the $(La_{1-x}Sr_x)(Cr_{1-y}Ti_y)O_3$ material of the present invention when x was fixed at 0.2 and y was varied;

Fig. 10 is a graph showing changes in the reductive expansion of the $(La_{1-x}Sr_x)(Cr_{1-y}Ti_y)O_3$ material of the present invention when y was fixed at 0.1 and x was varied;

Fig. 11 is a graph showing changes in the electric conductivity of the $(La_{1-x}Sr_x)(Cr_{1-y}Ti_y)O_3$ material of the present invention when y was fixed at 0.1 and x was varied; and

Fig. 12 is a graph showing changes in the coefficient of thermal expansion of the $(La_{1-x}Sr_x)(Cr_{1-y}Ti_y)O_3$ material of the present invention when y was fixed at 0.1 and x was varied.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to clarify the effects of the present invention, the following examples are given.

Example 1

A series of oxides having a composition represented by the following general formula were experimentally prepared: $(La_{1-x}Sr_x)(Cr_{1-y}Zr_y)O_3$, where x is in the range of 0 to 0.5 and y is in the range of 0 to 0.4.

Lanthanum oxide, strontium carbonate, chromium oxide, and zirconium oxide, which were used as starting powders, were mixed according to several formulations. Each of mixtures was blended in a ball mill and then heat-treated at 1,300°C for 10 hours to obtain a compound oxide powder. Then, the compound oxide powder was uniaxially pressed at 100 kg/cm^2 to obtain a disk having a diameter of about 60 mm and a thickness of about 5 mm, which was subjected to CIP (cold isostastical press) at 2,000 kg/cm^2. The resulting compact was sintered at a temperature of 1,500-1,700°C to obtain a sintered compact. From the several discoid sintered compacts thus obtained, 3 x 4 x 40 mm test pieces were prepared and used as samples for the measurement of some physical properties. These physical properties were measured according to the following procedures.

[Reductive expansion]

Each test piece was maintained in an atmosphere of hydrogen at 1,000°C for 5 hours. After cooling, its change in length was measured.

[Electric conductivity]

Four platinum lead wires were wound around each test piece with the space of about 10 mm between adjacent lead wires. Then, its electric conductivity was measured at various temperatures according to the direct-current four-terminal method.

[Coefficient of thermal expansion]

While the temperature of each test piece was raised at a rate of 10 °C/min, its thermal expansion was measured continuously.

Fig. 1 shows data on the reductive expansion. The abscissa indicates the value of y in the above general formula and the ordinate the reductive expansion (%). In

this case, the value of x in the above general formula was fixed at 0.2.

When y = 0, the reductive expansion is as high as 0.3%. Even if x = 0.2, as the value of y is increased from 0, the reductive expansion becomes lower.

Fig. 2 shows data on the electric conductivity at 1,000°C. The abscissa indicates the value of y in the above general formula and the ordinate the electric conductivity ($S \cdot cm^{-1}$). Also in this case, the value of x in the above general formula was fixed at 0.2.

When y = 0, the electric conductivity is as high as 37 $S \cdot cm^{-1}$. However, the electric conductivity becomes lower as the value of y is increased from 0.

Fig. 3 shows data on the coefficient of thermal expansion. The abscissa indicates the value of y in the above general formula and the ordinate the coefficient of thermal expansion ($x\ 10^{-6}\ °C^{-1}$). Also in this case, the value of x in the above general formula was fixed at 0.2.

When y = 0, the coefficient of thermal expansion is $10.3 \times 10^{-6}\ °C^{-1}$ and almost equal to that of YSZ (i.e., $10.3 \times 10^{-6}\ °C^{-1}$). However, the coefficient of thermal expansion becomes lower as the value of y is increased.

The above-described results have revealed that, when the value of y (i.e., the proportion of Cr which is replaced by Zr) is increased, the reductive expansion becomes lower, but the electric conductivity and the coefficient of thermal expansion also become lower.

Fig. 4 shows data on the reductive expansion. The abscissa indicates the value of x in the above general formula and the ordinate the reductive expansion (%). In this case, the value of y in the above general formula was fixed at 0.1.

When y = 0.1, the reductive expansion becomes higher as the value of x is increased.

Fig. 5 shows data on the electric conductivity at 1,000°C. The abscissa indicates the value of x in the above general formula and the ordinate the electric conductivity ($S \cdot cm^{-1}$). Also in this case, the value of y in the above general formula was fixed at 0.1.

When x = 0, the electric conductivity is as low as 1 $S \cdot cm^{-1}$. However, the electric conductivity becomes higher as the value of x is increased.

Fig. 6 shows data on the coefficient of thermal expansion. The abscissa indicates the value of x in the above general formula and the ordinate the coefficient of thermal expansion ($x\ 10^{-6}\ °C^{-1}$). Also in this case, the value of y in the above general formula was fixed at 0.1.

When x = 0, the coefficient of thermal expansion is $7.5 \times 10^{-6}\ °C^{-1}$ and significantly lower than that of YSZ (i.e., $10.3 \times 10^{-6}\ °C^{-1}$). However, the coefficient of thermal expansion becomes higher as the value of x is increased.

The above-described results have revealed that, when the value of x (i.e., the proportion of La which is replaced by Sr) is increased, the reductive expansion becomes higher, but the electric conductivity and the coefficient of thermal expansion also become higher.

Where the $(La_{1-x}Sr_x)(Cr_{1-y}Zr_y)O_3$ material is to be used in SOFCs and the like, it is necessary that its coef-

ficient of thermal expansion be almost equal to that of the solid electrolyte YSZ and, at the same time, it have a high electric conductivity and shows low reductive expansion. As a result, it has been concluded that the value of x should preferably be in the range of 0.1 to 0.2 and the value of y in the range of 0.05 to 0.2.

Example 2

A series of oxides having a composition represented by the following general formula were experimentally prepared: $(La_{1-x}Sr_x)(Cr_{1-y}Ti_y)O_3$ where x has a value in the range of 0 to 0.5 and y has a value in the range of 0 to 0.4.

Lanthanum oxide, strontium carbonate, chromium oxide and titanium oxide, which were used as starting powders, were mixed according to several formulations. Each of mixtures was blended in a ball mill and then heat-treated at 1,300°C for 10 hours to obtain a compound oxide powder. Then, the compound oxide powder was uniaxially pressed at 100 kg/cm² to obtain a disk having a diameter of about 60 mm and a thickness of about 5 mm, which was subjected to CIP treatment at 2,000 kg/cm². The resulting compact was sintered at a temperature of 1,500-1,700°C to obtain a sintered compact. From the several discoid sintered compacts thus obtained, 3 x 4 x 40 mm test pieces were prepared and used as samples for the measurement of some physical properties. These physical properties, such as the reductive expansion, electric conductivity, and coefficient of thermal conductivity, were measured in the same manner as in Example 1.

Fig. 7 shows data on the reductive expansion. The abscissa indicates the value of y in the above general formula and the ordinate the reductive expansion (%). In this case, the value of x in the above general formula was fixed at 0.2.

When y = 0, the reductive expansion is as high as 0.3%. Even if x = 0.2, as the value of y is increased from 0, the reductive expansion becomes lower.

Fig. 8 shows data on the electric conductivity at 1,000°C. The abscissa indicates the value of y in the above general formula and the ordinate the electric conductivity ($S \cdot cm^{-1}$). Also in this case, the value of x in the above general formula was fixed at 0.2.

When y = 0, the electric conductivity is as high as 37 $S \cdot cm^{-1}$. However, the electric conductivity becomes lower as the value of y is increased from 0.

Fig. 9 shows data on the coefficient of thermal expansion. The abscissa indicates the value of y in the above general formula and the ordinate the coefficient of thermal expansion ($x\ 10^{-6}\ °C^{-1}$). Also in this case, the value of x in the above general formula was fixed at 0.2.

When y = 0, the coefficient of thermal expansion is $10.3 \times 10^{-6}\ °C^{-1}$ and almost equal to that of YSZ (i.e., $10.3 \times 10^{-6}\ °C^{-1}$). However, the coefficient of thermal expansion becomes lower as the value of y is increased.

The above-described results have revealed that, when the value of y (i.e., the proportion of Cr which is

replaced by Zr) is increased, the reductive expansion becomes lower, but the electric conductivity and the coefficient of thermal expansion also become lower.

Fig. 10 shows data on the reductive expansion. The abscissa indicates the value of x in the above general formula and the ordinate the reductive expansion (%). In this case, the value of y in the above general formula was fixed at 0.1.

When y = 0.1, the reductive expansion becomes higher as the value of x is increased.

Fig. 11 shows data on the electric conductivity at 1,000°C. The abscissa indicates the value of x in the above general formula and the ordinate the electric conductivity ($S\cdot cm^{-1}$). Also in this case, the value of y in the above general formula was fixed at 0.1.

When x = 0, the electric conductivity is as low as 1 $S\cdot cm^{-1}$. However, the electric conductivity becomes higher as the value of x is increased.

Fig. 12 shows data on the coefficient of thermal expansion. The abscissa indicates the value of x in the above general formula and the ordinate the coefficient of thermal expansion ($x\ 10^{-6}\ °C^{-1}$). Also in this case, the value of y in the above general formula was fixed at 0.1.
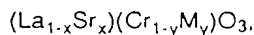
When x = 0, the coefficient of thermal expansion is $7.5 \times 10^{-6}\ °C^{-1}$ and significantly lower than that of YSZ (i.e., $10.3 \times 10^{-6}\ °C^{-1}$). However, the coefficient of thermal expansion becomes higher as the value of x is increased.

The above-described results have revealed that, when the value of x, i.e., the proportion of La which is replaced by Sr, is increased, the reductive expansion becomes greater, but the electric conductivity and the coefficient of thermal expansion also become higher.

Where the $(La_{1-x}Sr_x)(Cr_{1-y}Ti_y)O_3$ material is to be used in SOFCs and the like, it is necessary that its coefficient of thermal expansion be almost equal to that of the solid electrolyte YSZ and, at the same time, it have a high electric conductivity and shows low reductive expansion. As a result, it has been concluded that the value of x should preferably be in the range of 0.1 to 0.2 and the value of y in the range of 0.05 to 0.2.

Claims

1. An interconnector material for use in electrochemical cells having Y_2O_3-stabilized ZrO_2 as a solid electrolyte, said interconnector material comprising a lanthanum chromite material having a general formula:

$$(La_{1-x}Sr_x)(Cr_{1-y}M_y)O_3,$$

where M is Zr or Ti, x is in a range of 0.1 to 0.2, and y is in a range of 0.05 to 0.2.

2. The interconnector material claimed in claim 1, a thermal expansion coefficient of which is approximately equal to that of yttria-stabilized zirconia used as a solid electrolyte in an electrochemical cell.

3. The interconnector material claimed in claim 1, a reductive expansion of which is about 0.1 % or less.

4. The interconnector material claimed in claim 1, wherein x is between 0.15 and 0.2, and y is between 0.1 and 0.15.
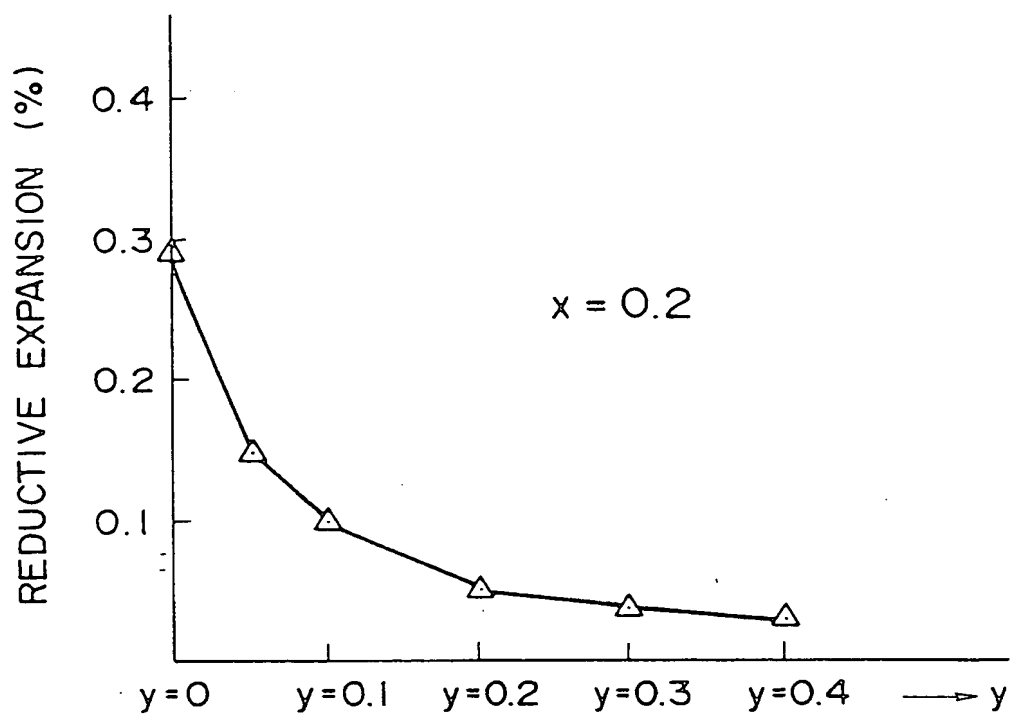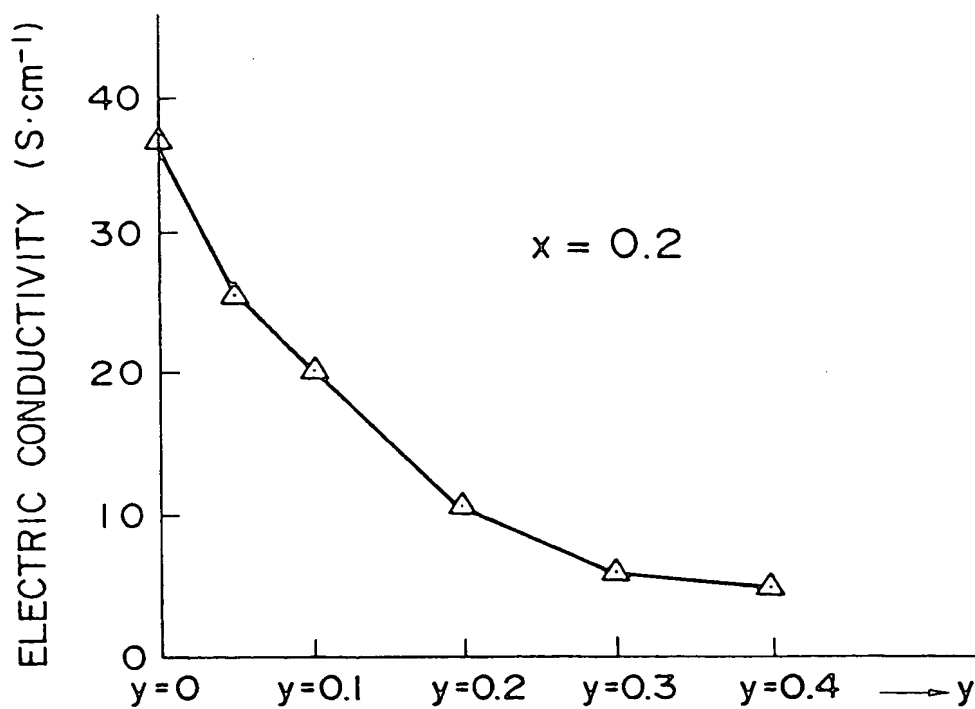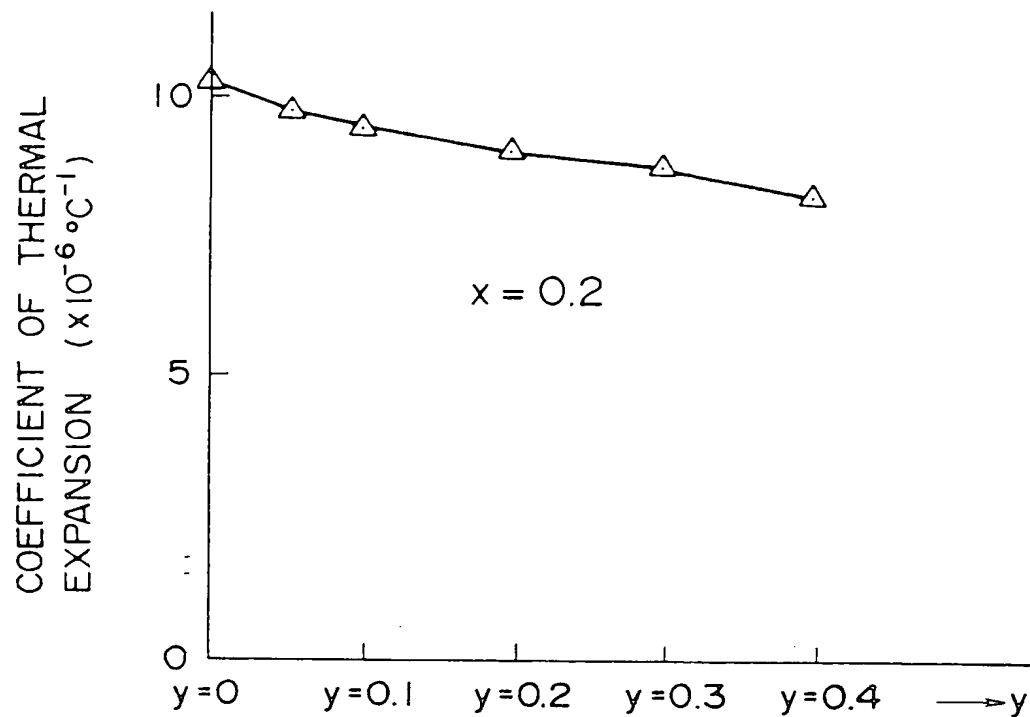
FIG. 1

x = 0.2

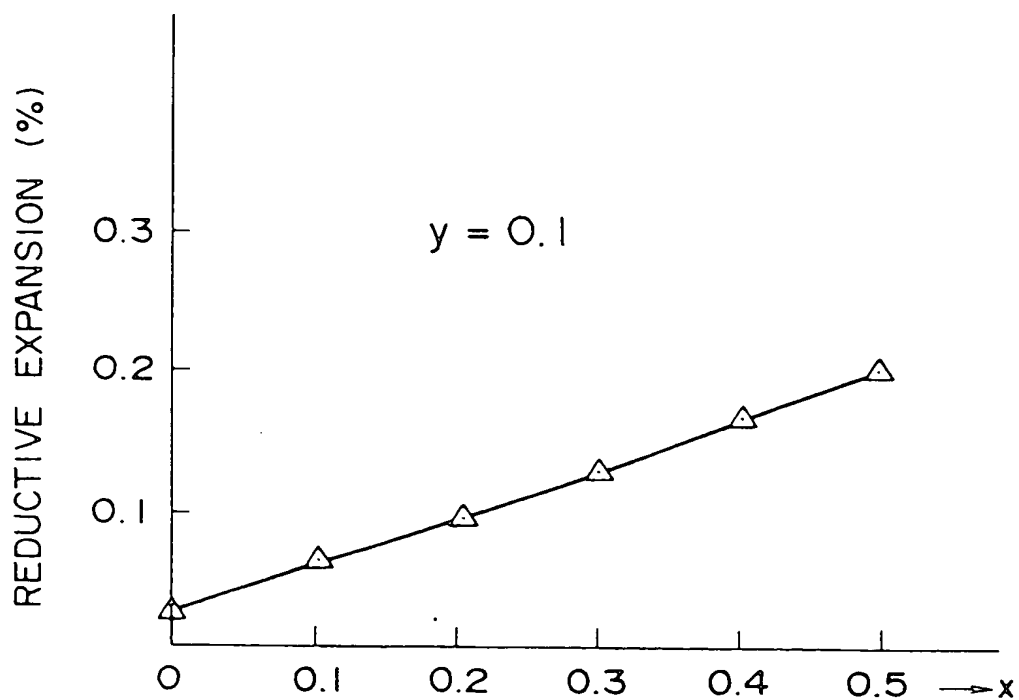REDUCTIVE EXPANSION (%) vs y

y=0   y=0.1   y=0.2   y=0.3   y=0.4   → y

FIG. 2

x = 0.2

ELECTRIC CONDUCTIVITY (S·cm⁻¹) vs y

y=0   y=0.1   y=0.2   y=0.3   y=0.4   → y

F I G . 3

F I G . 4

F I G. 5

y = 0.1

Axis labels: ELECTRIC CONDUCTIVITY (S·cm⁻¹) with values 10, 20, 30, 40; x-axis 0, 0.1, 0.2, 0.3, 0.4, 0.5 → x

F I G. 6

y = 0.1

Axis labels: COEFFICIENT OF THERMAL EXPANSION (×10⁻⁶ °C⁻¹) with values 0, 5, 10; x-axis 0, 0.1, 0.2, 0.3, 0.4, 0.5 → x

F I G. 7

F I G. 8

F I G. 9

x = 0.2

COEFFICIENT OF THERMAL EXPANSION ($\times 10^{-6}\,°C^{-1}$)

y = 0   y = 0.1   y = 0.2   y = 0.3   y = 0.4   ⟶ y

F I G. 10

y = 0.1

REDUCTIVE EXPANSION (%)

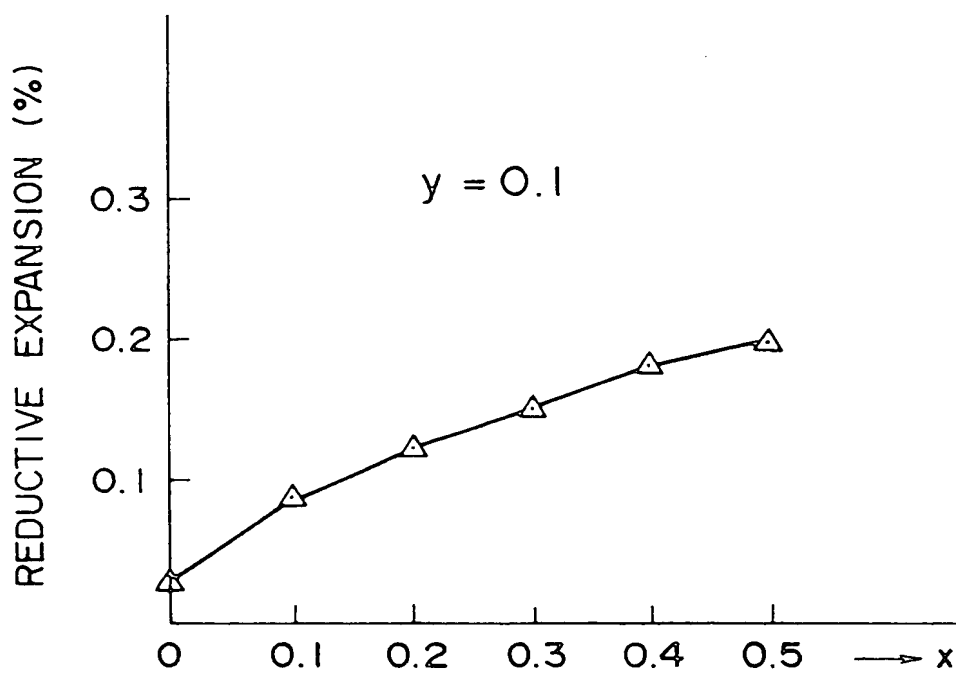0   0.1   0.2   0.3   0.4   0.5   ⟶ x
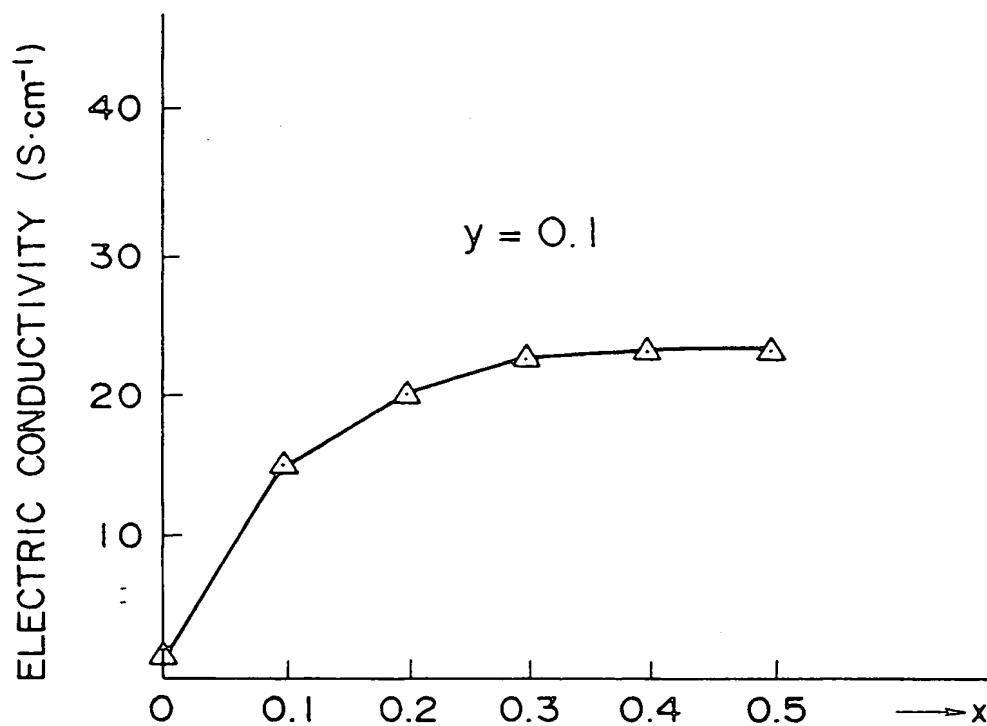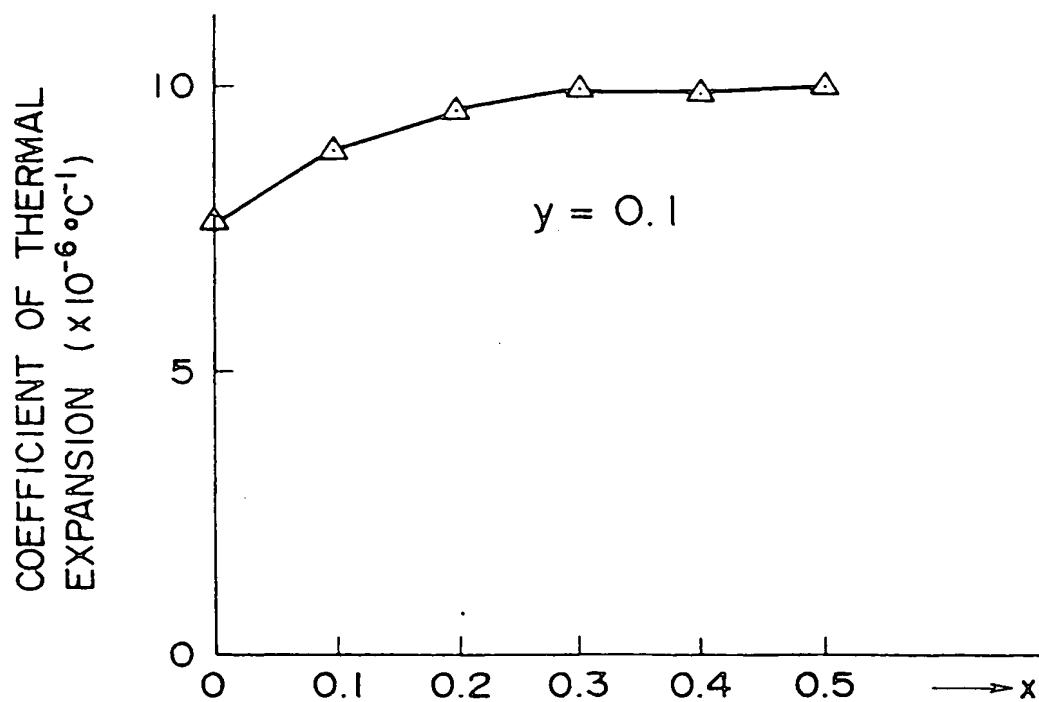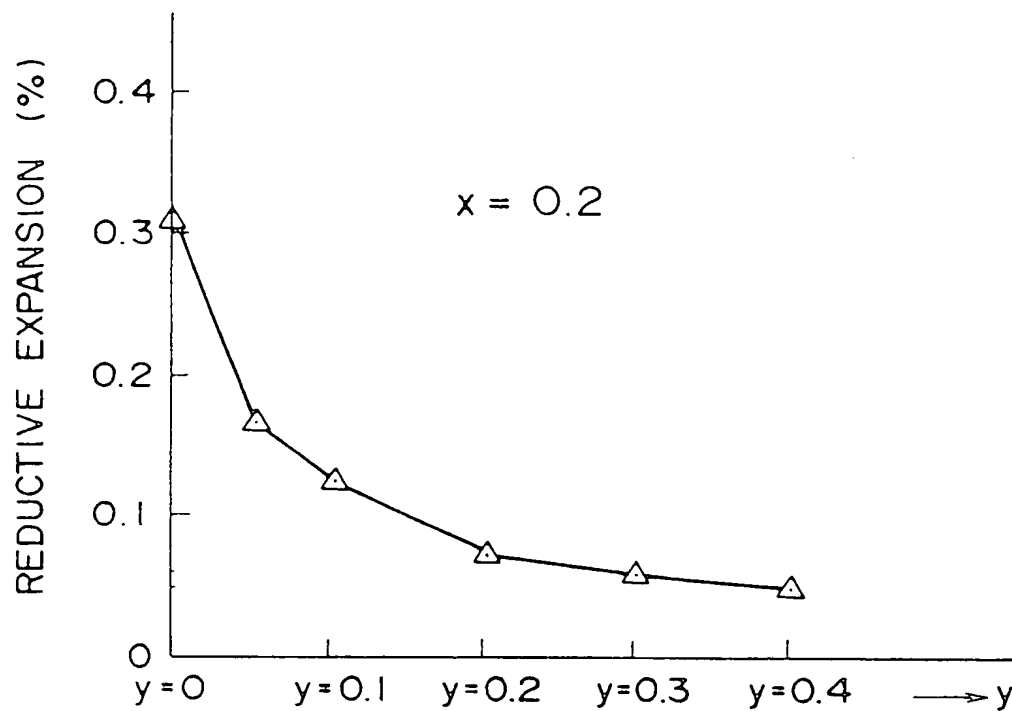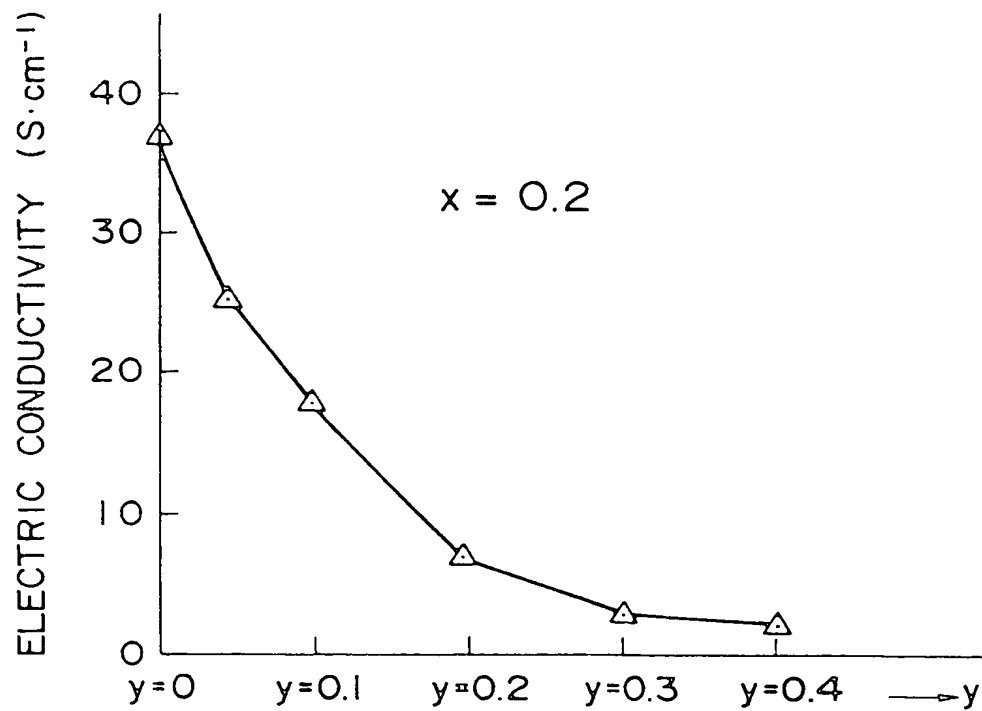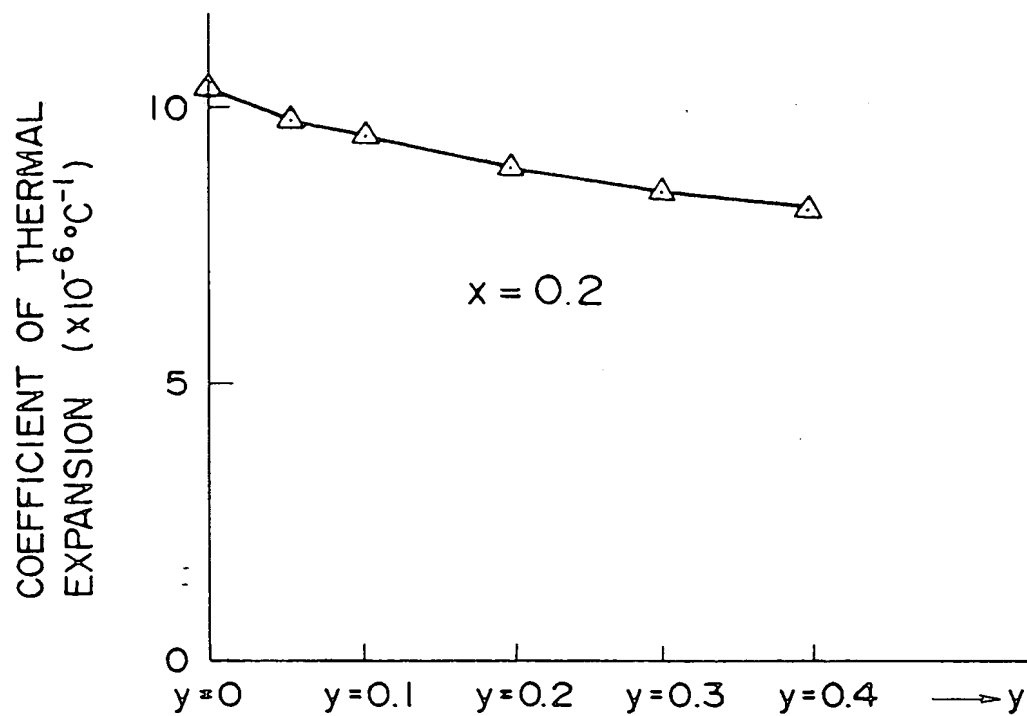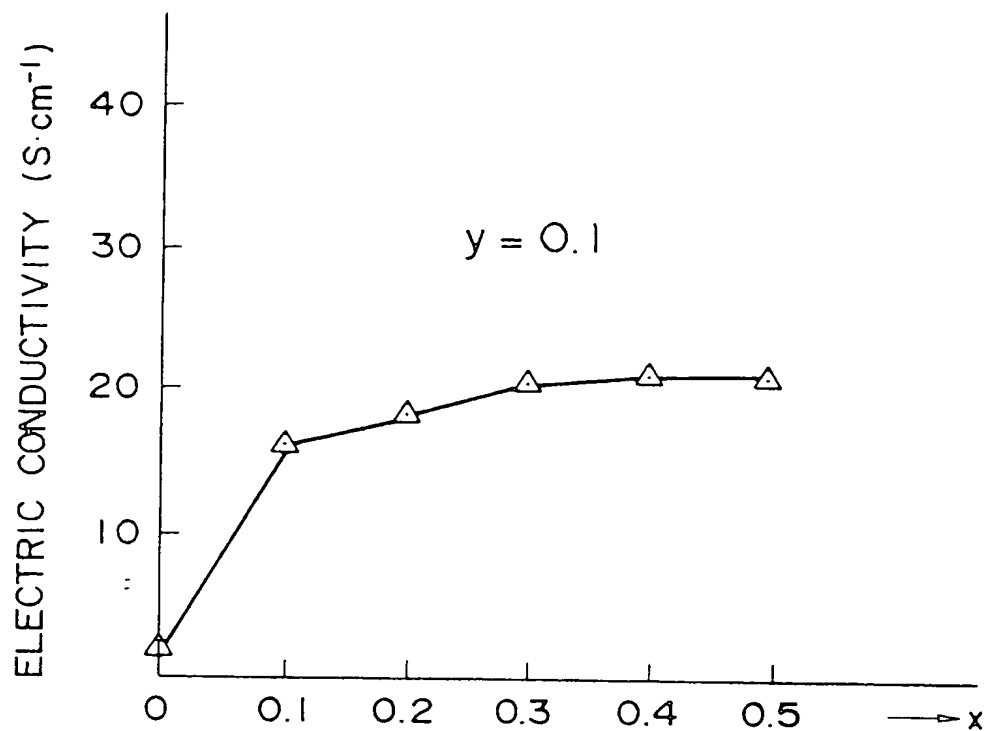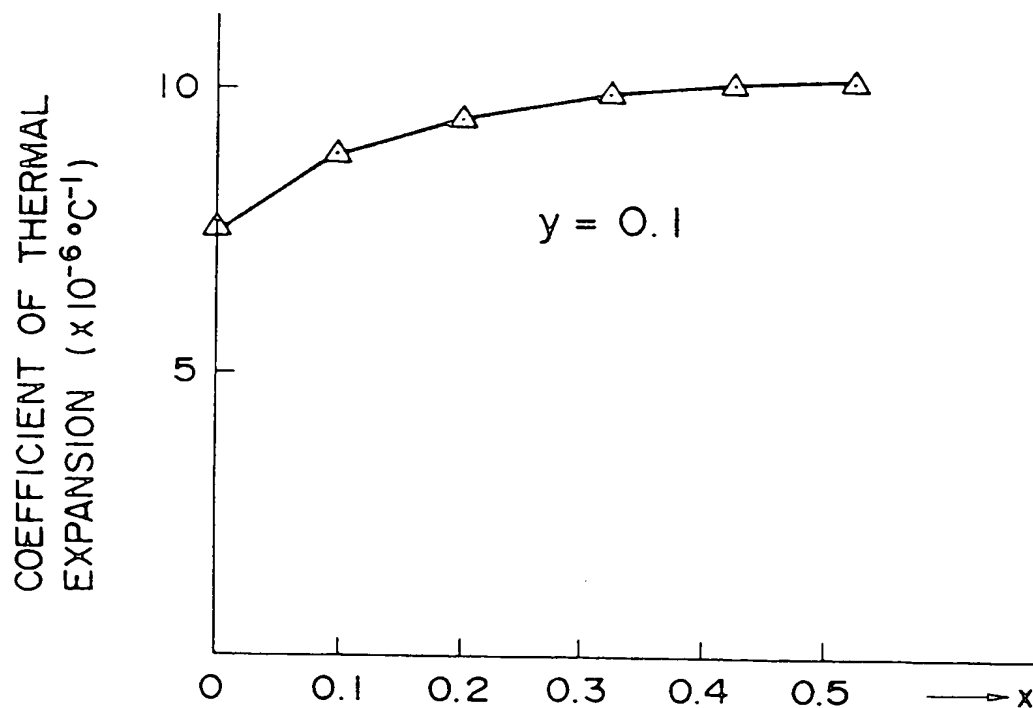
F I G. 11

F I G. 12

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 95 11 2696

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 018 no. 588 (C-1271) ,10 November 1994 & JP-A-06 219834 (TONEN CORP;OTHERS: 01) 9 August 1994, * abstract * * page 4; example 1; table 1 * ---	1,2,4	H01M8/02 C04B35/42 H01B1/08
X	PATENT ABSTRACTS OF JAPAN vol. 018 no. 344 (C-1218) ,29 June 1994 & JP-A-06 081062 (TONEN CORP;OTHERS: 01) 22 March 1994, * abstract * * page 4; example 1; table 1 * ---	1,2,4	
X	CHEMICAL ABSTRACTS, vol. 120, no. 4, 24 January 1994 Columbus, Ohio, US; abstract no. 34543, IWASAKI, HIROYUKI ET AL 'Densified composites and their manufacture' * abstract * & JP-A-05 178 664 (TONEN CORP, JAPAN;PETROLEUM ENERGY CENTER FOUND) * page 4; example 6; table 1 * ---	1,2,4	TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01M C04B H01B
P,X	CHEMICAL ABSTRACTS, vol. 122, no. 14, 3 April 1995 Columbus, Ohio, US; abstract no. 165560, AKYAMA, MASAHIDE 'Materials for solid electrolyte fuel cells' * abstract * & JP-A-06 302 326 (KYOCERA CORP, JAPAN) ---	1	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 October 1995	D'hondt, J

EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 95 11 2696

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	CHEMICAL ABSTRACTS, vol. 123, Columbus, Ohio, US; abstract no. 204345, AKYAMA, MASAHIDE ET AL 'Electroconductive ceramics and their manufacture, and current collectors using them for solid-electrolyte type fuel cells' * abstract * & JP-A-07 130 384 (KYOCERA CORP, JAPAN)	1	
A	CHEMICAL ABSTRACTS, vol. 118, no. 16, 19 April 1993 Columbus, Ohio, US; abstract no. 150931, GAMANOVICH, N. M. ET AL 'Electrically conducting contact material for a high-temperature fuel cell' * abstract * & VESTSI AKAD. NAVUK BELARUSI, SER. KHIM. NAVUK (1992), (5-6), 3-5 CODEN: VAKNEK, 1992	1	
A	EP-A-0 562 411 (NGK INSULATORS LTD) 29 September 1993 * claims 1,4 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP-A-0 395 400 (NGK INSULATORS LTD) 31 October 1990 * claims 1-4 * * page 10; table 2C *	1	
A	FR-A-2 315 151 (ARITA KOSHI) 14 January 1977 * page 6, line 9; claims 1-3 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 October 1995	D'hondt, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)